Development of Perpendicularly Magnetized L10-Mn1-xCoxAl (x=0,0.03) Thin Films for Electrodes of Magnetic Tunnel Junction

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URL	http://hdl.handle.net/10097/00127600

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授　与　学　位	博士（工学）
学位授与年月日	平成31年３月２７日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）応用物理専攻
学位論文題目	Development of Perpendicularly Magnetized $L1_0$-$Mn_{1-x}Co_xAl$ (x = 0, 0.03) Thin Films for Electrodes of Magnetic Tunnel Junctions
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論 文 内 容 要 旨

The $L1_0$-ordered alloys are an ideal ferromagnetic material with high perpendicular magnetic anisotropy (PMA) energy for spintronic applications. Among $L1_0$-ordered alloys, MnAl does not contain the heavy metals found in other $L1_0$-ordered materials. Therefore, MnAl has long spin diffusion length making it a very attractive and economical material for spintronics devices. Ferromagnetic MnAl thin films with PMA have also great interest in high-density storage, such as magneto-resistive random access memory (MRAM). For the spin-transfer-torque-type-MRAM (STT-MRAM), a thermal stability factor, $\Delta = K_uV/k_BT$, is required to be more than 60 for data retention for at least 10 years, where K_u and V are the magnetic anisotropy energy and the volume of ferromagnetic free layers in magnetic tunnel junctions (MTJs), respectively. Since the reduction of the size of the MTJs cell is required to achieve a high density, perpendicularly magnetized materials with the high K_u are required. In addition, the switching current density (J_{c0}) is expressed as J_{c0} ~

$\alpha M_s t H_k$, where α, M_s, t, and H_k are the magnetic damping constant, magnetization, thickness, and anisotropy field for ferromagnetic layers, respectively. Therefore, ferromagnetic thin films with high K_u, small M_s, and small α are needed to achieve both high thermal stability and low switching current. In this work, I focus on the $L1_0$-MnAl alloy which exhibits high K_u (1.5×107 erg/cc), a small M_s (550 emu/cc) and small α (0.006) for application of STT-MRAM. However, fabrication conditions of MnAl films are tightly restricted because the $L1_0$-ordered structure is a metastable phase. In previous work, a very high K_u and small M_s were observed in MnAl films prepared by a sputtering technique; however, the surface roughness of the films was large due to the high substrate temperature. The TMR ratio is very sensitive to the surface roughness of both the magnetic electrode and the insulating layer because the smooth surface would lead to more efficient coherent tunneling and a high MR ratio. Therefore, the reduction of the surface roughness is quite important to apply MnAl films to electrodes of MTJs. For MnAl thin films, reduction of preparation temperature is useful to improve the surface roughness of the films. It is possible to fabricate $L1_0$-MnAl films at low preparation temperature by substitution of Co atoms. In addition, Co-substitution onto MnAl can be decreased the magnetization due to the anti-ferromagnetic coupling between Mn and Co atoms. In this work, I fabricated MnAl and Co-doped MnAl thin films and systematically investigated structural and magnetic properties to decrease the surface roughness, while keeping the high perpendicular anisotropy.

$Mn_{1-x}Co_xAl$ films (x = 0, 0.03) were fabricated on MgO (100) single crystal substrates. The stacking structure for characterizing of $Mn_{1-x}Co_xAl$ films was MgO(100)-substrate/$Cr_{90}Ru_{10}$ (40)/ $Mn_{1-x}Co_xAl$ (3-50)/Ta (5). All the films were prepared using a magnetron sputtering system with a base pressure under 4×10^{-7} Pa. For the $Mn_{1-x}Co_xAl$ films deposition, the Ar gas pressure and sputtering power were set as 0.5 Pa and

20 W. $Mn_{46}Al_{54}$ and $Mn_{44}Co_2Al_{54}$ alloy targets were respectively used for deposition of MnAl and Co-doped MnAl films. The substrate temperature (T_s) during deposition was varied from 200°C to 400°C, and the post-annealing temperature (T_a) was also varied from 200°C to 500°C. The $Cr_{90}Ru_{10}$ buffer layer was deposited at room temperature and annealed at 650°C. The CrRu has a bcc structure with a lattice constant a = 0.290 nm and the lattice constants of $L1_0$-MnAl bulk are a = 0.392 nm and c = 0.357 nm. The $Cr_{90}Ru_{10}$ buffer layer reduces the lattice constant mismatch from 6.41 to 3.90% between the MgO substrate and the $L1_0$-$Mn_{1-x}Co_xAl$ films and gives a very flat surface. All films were capped by 5-nm-thick Ta capping layers, which prevent surface oxidization. The crystal structure and surface morphology in MnAl films were characterized by X-ray diffraction (XRD) and atomic force microscope (AFM). The M–H curves were measured by using a superconducting quantum interference device (SQUID) and a vibrating sample magnetometer (VSM), respectively.

Both the $L1_0$-ordering parameter and the PMA increased with increasing substrate temperature and showed a maximum of around T_s = 350°C for MnAl films. The substrate heating can help the MnAl film to form the $L1_0$-ordered structure. With increasing substrate temperature, the crystallinity of MnAl films was also improved. However, the surface roughness increased with increasing substrate temperature. The large strain energy at the interface between MnAl and CrRu buffer layer may trigger the 3D-growth at a high substrate temperature**.** The post-annealing process was systematically investigated to improve the surface morphology and I found that the post-annealing process worked well to reduce the roughness of the MnAl films. $L1_0$-ordering parameter also increased at a high annealing temperature. Finally, the MnAl films with both a very high K_u of 13 Merg/cc and relatively small surface roughness of 0.34 nm have been successfully obtained by using low substrate temperature of 250°C and high post-annealing temperature of 350°C.

For the free layer of STT-MRAM devices, the thickness of the films should be minimized in order to reduce the critical current density. For MnAl films, the thickness was successfully reduced down to 3 nm using optimized fabrication conditions (T_s = 250°C and T_a = 350°C) keeping perpendicular magnetic anisotropy. Although a magnetic dead layer of 2.7 nm was observed due to Ta and CrRu diffusion into MnAl interfaces in TEM images, the effective value of K_u = 6 Merg/cc was obtained for the 5-nm-thick MnAl film.

Although the roughness of the MnAl films was improved, the minimum surface roughness of 0.34 nm was slightly high for MTJs applications. In order to reduce the surface roughness, a small amount of Co was doped onto MnAl films. As a result, the surface roughness of Co-doped MnAl films was improved as 0.2 nm due to the suppression of the columnar growth by low growth temperature below T_s = 300°C. In addition, $L1_0$-ordered films were obtained at a low substrate temperature above T_s = 200°C. For Co-doped MnAl films, the post-annealing process was also investigated. The $L1_0$-ordering and magnetic properties in Co-doped MnAl films were improved by post-annealing keeping good surface morphology. Additionally, magnetization slightly decreased by Co-doping may due to anti-ferromagnetic coupling between Mn and Co atoms. The Co-doped MnAl films prepared by optimized conditions showed a very high K_u of 9.1 Merg/cc, small M_s of 475emu/cc and small roughness of 0.2 nm.

In summary, I found that post-annealing process with high temperature after the $Mn_{1-x}Co_xAl$ film growth with low substrate temperature was greatly useful for the fabrication of $L1_0$-ordered films with high K_u, small M_s and small surface roughness. In addition, Co-doping is also effective to reduce the surface roughness of

MnAl films. The obtained Co-doped MnAl films with very high K_u of 9.1 Merg/cc, small M_s of 475emu/cc, and small roughness of 0.2 nm will be greatly useful for next-generation STT-MRAM devices, which is expected to show high thermal stability of 67 and small switching current density J_{c0} of 2.9×10^6 A/cm^2.

(a) (b)

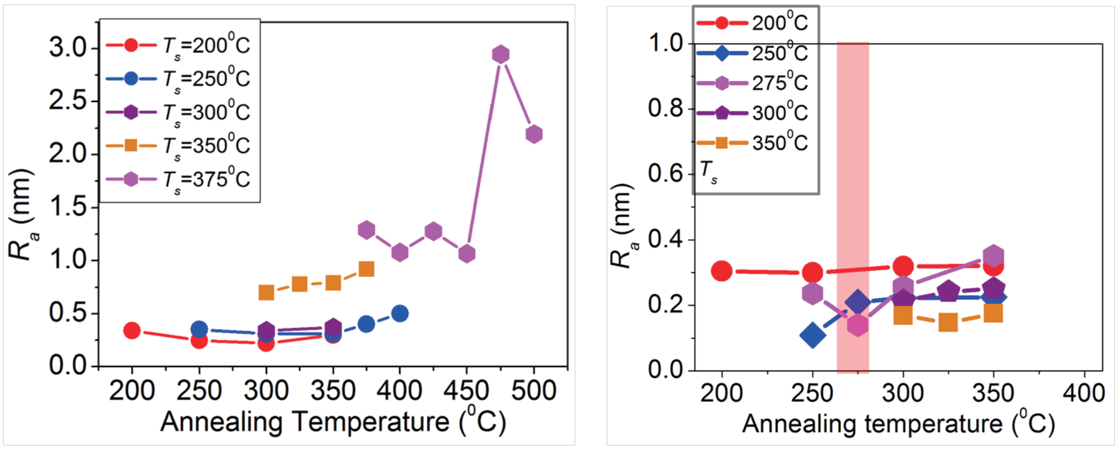

Figure: Effects of annealing temperature on surface roughness of (a)MnAl films and (b) MnCoAl films

論文審査結果の要旨

第 1 章は序論である。トンネル磁気抵抗効果、磁気メモリ、スピントランスファートルクなど、本論文に必要な研究背景に関して述べている。また、垂直磁気異方性を有する $L1_0$ 規則合金、特に MnAl と Co をドープした MnAl 合金に関して詳細にまとめ、目的と実現目標を掲げている。

第 2 章は実験方法である。薄膜の作製方法について述べている。また試料の評価方法として、表面粗さ、結晶構造、磁気特性などの測定方法について詳細を述べている。

第 3 章は $L1_0$ 規則の MnAl 薄膜の作製時の温度の最適化について述べている。$L1_0$ 規則 MnAl は τ 準安定相であるため、作製温度条件の最適化が重要である。基板温度の上昇とともに、K_u および M_s は増加した。一方、膜作製後のアニーリングは、$L1_0$ 規則相を形成し、平坦な表面を得るのに有効な方法である。最適化により、0.96 の秩序パラメータ値が得られた。このときの条件は、基板温度（T_s）: 250℃、成膜後アニール温度（T_a）: 350℃、磁気異方性エネルギー（K_u）: 13 Merg / cc、表面粗さ（R_a）: 0.34nm、飽和磁化（M_s）: 497emu / cc となった。

第 4 章は $L1_0$ 規則の MnAl 薄膜の膜厚低減化について述べている。薄い MnAl（3~20 nm）膜は、規則化を容易に促進することができず、その結果、磁気異方性エネルギーK_{ueff}が減少する。MnAl (50 nm) 膜は 13 Merg/cc という非常に高い K_u を示した。 一方、薄い MnAl（5 nm）膜は 6.00 Merg/cc という比較的低い K_u を示し、飽和磁化も $L1_0$ 規則 MnAl のバルク値（550 emu / cc）よりも低くなった。この飽和磁化の減少は 2.7 nm の磁気的に不感な層によるものであった。TEM 像をみると、MnAl 界面において Ta（タンタル）が拡散していた。

第 5 章は $L1_0$ 規則の Co ドープ MnAl 薄膜の表面粗さの低減化について述べている。表面粗さを小さくするために、MnAl に Co をドープした。 MnAl への Co 置換は、高秩序の $L1_0$-MnAl 膜を製造することが可能である。低い T_s = 250℃および T_a=275℃で 0.22 nm の非常に平坦な表面粗さを得た。一方、Co 添加により飽和磁化は減少し、K_u も減少した。MnCoAl(50 nm) 膜に対して T_s = 250℃、T_a=275℃、K_u=9.1 Merg/cc、R_a =0.22 nm、M_s=475 emu/cc の結果を得た。これらから<20 nm ϕ の小さいサイズの p=MTJ に適用すると、67 の高い熱安定性および 2.9 MA/cm^2 の小さい電流密度に相当することを示した。

第 6 章は総括である。本論文において MnAlCo（2 nm）を p-MTJ 自由層として使用すると目標とする熱安定性と電流密度を満たすことを示すことができた。また本論文の付録において、実際にこれを用いた MTJ 作製を試み、簡単なシミュレーションによって結果を説明できることも示している。これらの一連の結果は高密度磁気メモリ実現に向けた重要な指針を得ることができた。得られた知見は、工学応用のみならず、応用物理学の発展に寄与する重要なものである。

従って本論文は博士(工学)の学位論文として合格と認める。